FINAL REPORT

STUDIES OF REACTION GEOMETRY IN OXIDATION AND REDUCTION OF THE ALKALINE SILVER ELECTRODE

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Eliot A. Butler

Chemistry Department

Brigham Young University

Provo, Utah

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INTRODUCTION

The report is divided into three major sections which describe the work of the contract period. The sections are: I. Oxidation of Sintered Silver Electrodes at Constant Potential (page 2); II. Charge Characteristics of Silver Electrodes at Constant Current (page 5); and III. Variations of Surface Potential in the Oxidation of Silver Electrodes at Constant Current (page 14).

I. Oxidation of Sintered Silver Electrodes at Constant Potential

Apparatus and Reagents

A Hewlett-Packard Model 881 AX Power Supply was used to supply a constant potential across the silver and the counter electrodes. A Leeds and Northrup Speedomax H Recorder wired across a 0.1 ohm resistor which was in series with the electrodes recorded the current as a function of time.

Experiments were made upon sintered silver electrodes (1 cm on an edge) from three different sources. Plates of 0.5 mm thickness were obtained from the Delco-Remy Company and plates of 0.4 mm thickness were obtained from the Yardney Company. Other plates were prepared in this laboratory by the following procedure: Silver powder, 99.9% pure, 600 mesh, was hand pressed (approximately 80 pound/cm^2) on expanded silver metal (Exmet 5 Ag 10-4/0) with paper masks being used for thickness control. These pressed plates were heated at 1100°F for 30 minutes. Plates were chosen which fell into either of two thickness ranges: 0.38-0.43 mm and 0.71-0.86 mm.

The experiments were made in 40% KOH solution. As is indicated in the Results and Discussions section below, in certain experiments the KOH solution was saturated with zinc oxide, while in others, no zinc oxide was present.

Either a platinum foil electrode or a zinc plated platinum electrode was used as the counter electrode. The electrode was 2 cm x 2.5 cm x 0.003 inch.

Results and Discussion

Current-time curves of the shape shown in Figure 2 were obtained in constant applied-potential experiments early in the work of this contract. The current rise which is observed after an initial rapid decrease in current appeared to be attributable to (a) an increase in effective electrolytic surface area as solution penetrates the pores of the sintered

plate or (b) to changes in the overpotential for the electrode reaction as the surface changes from silver metal to a thin layer of oxide. Therefore, experiments were made in an effort to determine the cause of the current rise. Curves of similar shape were obtained with silver electrodes of all three types used. Since no binder of any kind had been used in the plates prepared in this laboratory, those plates were used for the experiments reported here.

The platinum counter electrode was cleaned by dipping it in 12 F HCl and rinsing it thoroughly with distilled water. Cleaning the Pt between runs was not shown to have any benefit. The cell solution was used for two or a maximum of three runs. The magnitude of the applied potential was chosen as a function of the reaction which occurred at the cathode, that potential being selected which caused significant observable oxidation of Ag to Ag_2O, but which was too low for oxidation of Ag_2O to AgO. The cathode reaction was different depending upon whether or not ZnO was present in the electrolyte.

Unsoaked plates were oxidized in 40% KOH at applied potential 1.475 v. with a Pt counter electrode. The current-time curve showed a current rise of short duration following the initial sharp decrease (Fig. 2). Plates soaked 1-2 hours were similarly oxidized, giving a curve in which there was a much smaller current rise or a short plateau (Fig. 3). The rise or plateau appeared in all experiments. The two curves in Figure 3 show the extremes of behavior of plates tested. A third series of unsoaked plates was oxidized in 40% KOH saturated with ZnO at constant potential 1.750 v. The Zn was plated on a Pt electrode. Two groups of runs were made, one using a cleaned Pt plate each time and the other using the same Zn-coated electrode each time. All runs showed a current rise as before, the rise lasting somewhat longer in runs using the Zn-coated electrode (Fig. 4). Finally a series of plates soaked 1-3 hours was oxidized at 1.750 v. in 40% KOH saturated with ZnO using a Zn-plated Pt electrode. Soaking the plates did not decrease the current rise (Fig. 5). Stirring the solutions did not effect the current rise.

Since soaking the plates was shown to affect the current rise for one cathodic reaction, but not for the other, it appears that the current rise results from effects at both the anode and the cathode.

It should be noted that the soaking of a sintered silver plate for a period of hours did not remove the current rise which appeared in a matter of minutes. It appears, therefore, that the current rise is not caused only by an increase in effective surface area by the penetration of electrolyte into the pores of the electrode but must depend also upon other changes such as, perhaps, a change in overpotential for oxidation of Ag as the surface is changed through reaction.

The fact that stirring the solution did not change the current-time curve indicates that the change in reaction which causes the current rise must occur at or very near the solution-electrode interface.

II. Charge Characteristics of Silver Electrodes at Constant Current

Apparatus and Reagents

Constant current was supplied for these experiments by means of a bank of batteries (Type B 224/U) in series with sufficient resistance to provide the current of desired magnitude. The current was measured as the potential drop across a standard resistor in series with the working cell. Currents ranging in magnitude from 2 microamps to 1 milliamp were obtained which were constant to within 2%. The potential of the silver cell was measured versus a Hg-HgO electrode with a Varian recording potentiometer. The silver plates used in these experiments were of silver foil (0.1 mm thickness) cut to various sizes. The silver wire which was welded onto the silver electrode was 0.57 mm diameter and of 99.9% purity. The counter electrode was a 2 x 3 cm piece of platinum foil. The reference electrode was prepared by grinding 99.9% mercury together with reagent grade HgO in an agate mortar. This HgO-coated mercury was then transferred to the working cell which was fitted with a platinum connection wire. The electrolyte was approximately 0.1 N KOH with about 1% $CO_3^=$ contamination. The electroplating solutions were prepared with reagent grade chemicals in the manner prescribed by Mohler and Sedusky.[1] Constant current for the electroplating was provided by a 6 volt battery in series with sufficient resistance to give the desired current.

In the polishing process, several kinds of wheels and rouges were used. The buffing wheels included a felt polishing wheel, a coarse muslin buffing wheel, and a fine buffing wheel. They were used in connection with HR Superior Red Rouge #52-422 and a special polishing compound Dremel #A-21. for polishing metals. An ultrasonic cleaner Disontegrator, System 40 was used to some extent in the cleaning process. (Ultrasonic Industries, Inc. Model G 40 C1 P-16, Serial #15384.)

EXPERIMENTAL TECHNIQUES

Oxidation Runs

In all cases, the oxidation runs were made in the following way: The silver electrode to be oxidized was placed in the cell and supported at a

constant depth in the cell solution. It was made the reducing electrode for a period of about 2 minutes before the polarity was reversed and the oxidation begun. The potential was recorded continuously and the current was measured periodically. In the study of the peak characteristics, the oxidation was continued until the potential necessary for the evolution of oxygen was reached. In the study of surface area determination, the oxidation was stopped shortly after the peak labelled B in Fig. 6 appeared.

Electroplating

The electroplating solutions and procedures were patterned after those given by Mohler and Sedusky.[1] A constant current density of 1.33 ma/cm^2 was used and the electrodes were plated for about 2 hours. In some cases, the electrodes were made the reducing electrodes in a striking solution for 1 minute before being electroplated but no apparent benefit resulted so this was discontinued.

Storing of the electrodes

If the electrodes were to be stored before their use in oxidation runs, they were rinsed thoroughly with distilled water, allowed to dry, and stored in a desiccator until they were used.

OXIDATION OF SILVER ELECTRODES AT CONSTANT CURRENT

In the oxidation of silver electrodes at constant current, the potential of the silver electrode is observed to go through the changes shown in Fig. 6. The potential rises quite rapidly at first and then levels off, sometimes giving a small peak, to the plateau corresponding to the production of Ag_2O. At the end of this first plateau, the potential rises again, giving a definite peak before leveling off to the plateau corresponding to the production of AgO. At the end of this second plateau, the potential rises then to that value necessary for the evolution of oxygen. There are two particular points of the oxidation potential curve which are of interest in this report. The first is the occurrence of the peak labelled B in Fig. 6 and the second is the length of the first plateau which occurs between peaks labelled A and B on Fig. 6.

The peak labeled B on Figure 6 has been the subject of much controversy. It has been reported by various workers and has been given several explanations. Hickling and Taylor[2] reported it and attributed it to the formation of some higher, unstable oxide of silver which decomposed rapidly to form argentic oxide, AgO. Jones, Thirsk, and Wynne-Jones[3] have also reported this peak and they have offered as an explanation for it the difficulty of forming AgO nuclei in the Ag_2O layer. Dirkse and Werkema[4], however, have attempted to explain this peak by the extraordinarily high resistance of the lower oxide, Ag_2O, as compared to that of the higher oxide, AgO. Also, in another study, Dirkse[5] suggested that perhaps the distortion of the cubic arrangement of the silver atom or ion to form Ag(II) could be responsible for the peak. In a more recent study by Cahan, Ockerman, Amlie and Ruetschi,[6] it has been reported that the resistance of the oxides alone cannot explain the peak since the potential change at the peak is much greater than that possible if the ohmic resistance were the only factor considered. This report goes on to account for the peak in terms of the passivation of the plate at the instant of complete coverage by the highly resistive Ag_2O when the current flow is forced to very limited areas of unreacted silver and the overvoltage is therefore extremely high. Wales and Burbank[7] showed the presence of this peak in the oxidation curves which they obtained in their study, but they did not attempt any explanation for its presence. They did, however, report that the X-ray diffraction studies which they made showed no evidence of any oxide higher than AgO. Our work has shown that this peak has been present in all experiments at current densities ranging from 0.2 ma/cm^2 to 15 ma/cm^2, although it varies with changes in current density, becoming sharper and reaching a higher maximum with higher current densities. This peak (B) also changed somewhat in appearance in cycling experiments. These cycling experiments consisted of taking a silver electrode, oxidizing it until the potential necessary for oxygen evolution was reached and then reversing the polarity and reducing the Ag oxides until the potential for hydrogen evolution was reached. This procedure was then repeated on the same

electrode until three complete cycles were obtained. The peak height decreased somewhat and the width increased in the second and third cycles.

Effects of Surface Area

It has been suggested by several workers[6, 8] that the first plateau of the oxidation curve corresponds to the covering of available surface area with a thin layer (perhaps monolayer) of Ag_2O. In a series of experiments in which plates of the same surface area were oxidized at various current densities and the lengths of the first plateau compared, it was found that if the current density is kept the same, the quantity $\frac{t \times I}{a}$ is constant. In this expression, t is the time in seconds which corresponds to the length of the plateau, I is the current in milliamps which flows and a is the area of the silver plate. In the cases in which unpolished or polished plates were used. the surface area was taken as the calculated geometric surface area. This quantity $\frac{t \times I}{a}$ was found to take on a different constant value at each different current density but when a plot was made of $\frac{t \times I}{a}$ against $\frac{I}{a}$, the smooth curve of Fig. 7 was obtained. When the $\log \frac{t \times I}{a}$ was plotted against $\frac{I}{a}$, the almost straight line of Fig. 8 was obtained. With this information, a possible method for determining effective surface area is suggested. This method is discussed below under "Surface Area Estimation."

In the cycling experiments, it was observed that on the second and third cycles with the polished silver plates, the effective surface area increased. It appears that in the oxidation and reduction of the polished silver plate, the arrangement of the silver atoms is sufficiently distorted and altered so that the effective surface area of the plate is increased and thus the plateau is lengthened.

As was indicated previously, there are two principal arguments which have been given for the existence of the peak labeled B in Fig. 6. These are (1) the high resistance of Ag_2O and (2) passivation resulting in very high current densities as last of the surface silver is oxidized. Perhaps a better term for this "passivation" is non-ohmic overpotential or activation overpotential. In our experiments, it was observed that the length of the plateau was increased with subsequent oxidation-reduction

cycles, suggesting that the effective surface area had been increased as has been mentioned. Another effect was also observed on the second and third cycles of those experiments. This was the apparent lowering and broadening of peak B. Both of these observed phenomena are of interest.

Figure 9 shows a plot of area of unoxidized silver metal surface versus time for two plots of five-fold difference in surface area with the same total current applied. Current density on the small plate was 0.90 ma/cm^2 and on the large plate it was 0.18 ma/cm^2. These plots are drawn as straight lines connecting the initial geometric area at time = 0 to the time when peak B appears at which time the area is assumed to be zero. It can be noted that the slopes are very different. The area of the silver on the small plate (with higher current density) decreases much more rapidly than does the area of the silver on the larger plate.

It can be seen from Fig. 9 that while the area increases by a factor of 5 in going from the small plate to the larger one, the time of oxidation and thus, presumably, the number of equivalents of Ag_2O formed increases by a factor of greater than 8. Thus there appears to be about 1 1/2 times as much Ag_2O formed per unit area on the larger plate. In other words, as the current density decreases, the depth of the oxidation increases and more Ag_2O per unit area is produced forming a thicker oxide film on the silver surface.

While our experiments do not indicate whether resistance or overpotential is the primary cause of peak B, we believe that additional information from the surface area experiments may help to resolve this question.

Surface Area Estimation

The suggestion has been made above that an estimation of the surface area which is effective in the electrolytic charge of a silver plate might be made upon the basis of the elapsed time between points A and B in the potential-time curve (Figure 6). While the surface area of a sintered plate can be measured by various techniques, it would be far more valuable to be able to make the measurement by a technique which depends upon

electrolytic reaction, since the area effective in such reaction is the important area in controlling current densities. Experimental work has been concentrated upon determination of reproducibility of measurement of the length of the first plateau (A to B, Figure 6) at various current densities upon electrodes prepared in as identical a manner as possible. If thoroughly cleaned electrodes of silver foil are charged at constant apparent current densities ranging from 0.2 ma/cm^2 to 0.8 ma/cm^2 the reproducibility of length of the first plateau is to $\pm$ 10%. Table I shows the data obtained when such electrodes were oxidized at various current densities.

Microscopic examination of the cleaned silver foil electrodes showed such gross irregularities in the surface characteristics that an attempt was made to polish these electrodes in order to obtain more uniform surfaces, and hopefully, to gain reproducibility in the determinations of a base line for surface area determinations. Several methods were used in this attempt. Electrodes were polished to a mirror finish and then cleaned in an attempt to remove any of the substances used in the polishing before the oxidation runs were made. These runs showed a loss in reproducibility. Table II shows the data obtained when various sorts of electrodes were oxidized and the lengths of the plateau for A to B in Fig. 6 measured. Figure 1 shows the contrast between a cleaned silver foil electrode (A) and a polished silver electrode(B).

When these oxidized electrodes were examined under magnification, it was evident that the cleaning process had not been efficient in removing the substances encountered in the polishing process. There were definite spots which appeared to have been protected from any oxidation scattered over the electrodes. (See Fig. 22) Several methods were then tried to see if the substances could be removed from the electrode surface. The most effective of these methods was the use of an abrasive cleaner which of course destroyed the mirror finish on the polished plates. An attempt was made to prepare a smooth, uniform surface by electroplating a layer of silver onto a silver electrode. Although some of these electrodes appeared to plate very smoothly and uniformly and the results from the oxidation runs were promising (See Table II), consistently good plating was not achieved. Various attempts

Table I

Approximate Current μa	Measured Current (Total spread shown) μa	Apparent Current Density $\frac{ma}{cm^2}$	Length of First Plateau(seconds)	Deviation from Average
200	205.5 - 205.0	0.181	330	± 3%
	205.3 - 204.9		320	
	205.4 - 205.1		315	
300	309.5 - 308.9	0.273	135	
	309.5 - 308.7		140	
	309.4 - 307.8		150	
	309.4 - 307.8		155	± 7%
	309.2 - 307.7		140	
400	415.3 - 413.2	0.366	90	
	415.5 - 413.0		86	± 7%
	415.6 - 413.1		79	
	414.0 - 412.7		90	
500	510.0 - 508.7	0.451	64	
	511.0 - 508.8		60	± 7%
	511.1 - 508.5		56	
600	616.4 - 613.3	0.543	42	
	616.7 - 613.3		48	
	616.7 - 613.1		45	± 7%
700	700.0 - 697.5	0.619	39	
	701.0 - 697.3		41	
	700.8 - 696.9		37	± 7%
800	820.7 - 816.6	0.730	27	
	820.8 - 814.8		32	±10%
	820.7 - 815.5		30	

Table II

Type of electrode	Length of plateau	Deviation	Approximate Current
Cleaned, unpolished electrodes	135 sec 140 " 150 " 155 " 140 "	± 7%	0.30 ma
Polished electrodes, cleaned with a detergent in the ultrasonic cleaner	108 sec 105 " 93 " 107 " 106 " 124 " 126 "	±17%	0.30 ma
Polished electrodes, cleaned with CCl_4 and then with a detergent, in the ultrasonic cleaner	94 sec 128 " 141 " 135 " 109 "	±27%	0.30 ma
Polished electrodes, cleaned with abrasive cleaner, anodized for 30 minutes in plating solution and then electroplated for 2 hours	227 sec 223 " 219 " 210 " 220 "	± 4%	0.30 ma
Polished electrode, cleaned with abrasive cleaner and electroplated for 2 hours	156 sec 161 " 153 " 159 "	± 4%	0.30 ma

were then made to obtain good uniform plating. Some of these methods are:

a. Polished electrodes which had been cleaned with an abrasive cleaner were electroplated,

b. Unpolished electrodes which had been cleaned either with a detergent or the abrasive cleaner were electroplated in order to avoid the problem of the rouge used in polishing, and

c. Electrodes which had been slightly etched in HNO_3 (3 seconds in 8 N HNO_3) were electroplated.

Of these methods, the etched electrodes seemed to give the best results. It appears that the plating is consistently smooth and uniform but further work will be required to determine the reproducibility which can be obtained in the oxidation runs. In the case of the other methods, the electrodes were very non-uniform in the plating, showing definite edge effects as well as other evidences of non-uniformity.

PROPOSED WORK

Future work in this type of experiment will include attempts to find a technique for providing uniform surface areas of silver in the determination of a base line for surface area estimation as well as the application of such estimations to various kinds of silver surfaces once a base line has been established.

III. Variations of Surface Potential in the Oxidation of Silver Electrodes at Constant Current

During oxidation of Ag foil plates at low constant current density (.2 ma/cm^2) more rapid darkening occurred near the edge. Oxidation of Ag plates at high current densities, about 60 ma/cm^2, shows very clearly the initiation of oxidation at the edges and the movement of oxidation toward the center in a circle of diminishing radius. It is possible to observe the oxidation proceed from edge to center followed by the second stage of oxidation as shown by the change from brown to almost black, again starting at the edge and working to the center. Reduction of these plates shows the same pattern, lightening beginning at the edges and sweeping toward the center of the plate. Photomicrographs, Figs. 10, 11, 12, 13, 14, 15 were taken showing the darkening at the edges of plates partially oxidized at .2 ma/cm^2 and 60 ma/cm^2. This edge effect has also been observed by other authors. Hedges,[9] while oxidizing Cu and Ag plates noted that "whenever deposition of a film occurs in electrolysis, this starts at the sides and lower part of the electrode and travels up the electrode in the form of a U of diminishing concavity. This seems to be due to the concentration of current density at the corners and edges of the electrode..." Westermark[10] studying distribution of surface potential showed "that disks made of pure metals acquired uniform activity over the surface (apart from some edge effects)." Evans[11] oxidizing various metals found "there was a special tendency for the points of attack to lie near the edge of the specimen, where the metal had been stressed in cutting... Corrosion frequently started...on and very near the cut edges." Bannister and Evans[12] noted that the method they had previously used "allowed the liquid access to the cut edges of the vertical specimens, causing complications due to shearing stresses and exposure of the interior layers, which in rolled metals may differ physically and chemically from the face."

Other authors modify their electrodes in an attempt to maintain constant current density or constant potential over the surface of the electrodes. Eisenberg,[13] studying capillaries for overpotential measurement assumed the current distribution over the electrodes was uniform provided that "parallel planes connected by insulating planes normal to the electrodes" were used. Kasper,[14] discussing the theory of potential in electrodeposition, assumed that the surface of the electrodes were two infinite parallel plates to avoid any terminal affect.

Wagner,[15] prefacing a mathematical treatment of current density at the edges of an electrode stated, "In a rectangular electrolytic cell with plane electrodes parallel to each other and covering the end walls completely, the current density is in general the same at all points... [W]here the electrodes cover only a certain portion of the end walls... the current density at the edge of the electrodes is higher than that elsewhere." From the formula he derived, Wagner[15] graphed current density as a function of distance from the center of the electrode under various conditions. The conclusions have a direct application to our measurements since overpotential is a function of current density.

The difference in potentials at the center and edge of a Ag electrode may be due to (1) a purely geometrical effect (Wagner's argument), (2) the effect of shearing and other stresses, (3) a combination of the two. Our work has centered on an attempt to make accurate measurements of potential differences at center and edge.

Apparatus and Reagents

99.9% pure Ag sheets 1 cm^2 (thickness 0.004 in) cleaned by rubbing with acetone and rinsing in distilled H_2O were placed in the cell (Fig. 16) containing 0.1 N KOH (with 1% $CO_3^=$ contamination). One or two 67.5 v. batteries in series with large resistors (100-600 k ohm) provided the various currents used. The circuit is as diagrammed in Figure 18. The capillary was brought to the center of the Ag electrode and fixed at $<$ 0.3 mm from the plate. The potentials were measured with a Leeds and Northrup Universal K-3

potentiometer vs. a Hg-HgO electrode prepared by grinding reagent grade HgO and 99.9% Hg together. Initially, the Hg-HgO electrode was contained in an expanded portion of the capillary but later it was moved to the side of the cell and the solutions joined by a flexible connecting tube on the end of the capillary. This allowed the use of a relatively large Hg-HgO electrode which was found to be much more easily prepared and to have less variation in potential with time. In early experiments the circuit was broken between measurements but later experiments were made without interrupting the current flow. The ΔE from center to edge was found by noting the galvanometer deflection from the value of the potential measured at the center, when the capillary tip was moved to the edge. Then the ΔE from edge to center was similarly measured. The taking of measurements in both directions allowed us to make corrections for the slow potential rise due to increasing oxidation of the plate caused by the current flow. Although it is desirable to use a very fine capillary tip, we found that the resistance of the solution in the tip decreased the galvanometer sensitivity and limited the size of the tip which could be used. We selected a tip giving a sensitivity of 1 s.d./m.v. (0.3 mm). With the capillary tube approaching the Ag electrode from the front we noted some shielding on the Ag plates, but the shielding was assumed to affect both the E at the center and at the edge similarly. The method used initially to make the measurements involved the movement of the silver electrode with the capillary remaining fixed. Table III Runs No. (1, 2, 3, 4) shows data typical of those obtained by such a technique. Later measurements were made with the electrode fixed and with the capillary being moved.

EXPERIMENTAL RESULTS

The experimental results demonstrated several important relationships between the potential gradient (ΔE) over the test electrode surface and the following experimental variables:

1. Electrode configuration

Table III

Results of ΔE measurements on electrode configurations A, B, and C

Configuration A

Run	Current Density ma/cm^2	Material	Reaction	*x(mm)	**ΔE ave.	number of measurements	Standard Deviation
1	.2	Ag foil	oxidation	.3	1.4	11	.51
2	.2	Ag foil	oxidation	.3	1.0	3	.25
3	.2	Ag foil	oxidation	.3	1.0	4	.44
4	.2	Ag foil	oxidation	.3	2.0	11	.58
5	.2	Ag foil	oxidation	.3	1.0	2	0
6	.1	Ag foil	oxidation	3-4	0.5	5	.10
7	.1	Ag foil	reduction	.3	-1.0	5	.20
8	.1	Ag foil	oxidation	.3	1.0	5	.20

Configuration B

9	.1	Ag foil	oxidation	.3	1.0	5	.20
10	.1	Pt foil	oxidation	.3	1.0	5	.20
11	.1	Ag foil	oxidation	2-3	0.8	2	0
12	.1	Ag foil	oxidation	.3	1.4	6	.10
13	.1	Ag foil	reduction	.3	-1.3	6	.14
14	.1	Ag foil	oxidation	.3	1.7	17	.07
15	.13	Ag foil	oxidation	.3	1.1	10	.17
16	.05	Ag foil	oxidation	.3	0.4	14	.08

Configuration C

No results obtainable because of the difficulty in making measurements over a three-dimensional surface with the present apparatus. Such measurements required the simultaneous up or down motion of the test electrode and the in or out movement of the capillary sensing electrode. The time consumed in such movements made any ΔE small compared to the potential change due to the oxidation caused by the current flowing through the cell. Proposals for an improved test cell which would make such measurements possible are found on page 20 of this report.

** A + ΔE indicates a higher E at the edge (P_e) than at the center (P_c)

* X is the distance between the capillary tip and the electrode surface

2. Current density
3. Type of reaction occurring (oxidation or reduction)
4. Thickness of the oxide layer due to the electrode reaction
5. Position of the sensing electrode relative to the test electrode.

Three electrode configurations were tested. (See Figure 19).

Electrodes of configuration A were cut from sheet silver 0.004 inch thick and 99.99% pure. A silver lead wire of the same purity was pressure-welded to the top edge of these while being heated by a methane-air flame. The total surface area was 2-3 cm^2.

Electrodes of configuration B were fabricated in the same manner as configuration A except for the pointed edge. This edge was first roughly cut to shape and was then finished on a small hemispherical grinding wheel.

The cone-cylinder configuration of electrode C was turned from 3/8" brass rod and plated with silver at 1.3 ma/cm^2 for one hour. The procedure and solutions used were recommended by Mohler and Sedusky.[1]

As a test for a possible relationship between the radius of curvature at the edge of the plate and ΔE, the potential difference between center and edge, B and C were constructed -- B giving a decreased radius of curvature in a two dimensional body and C giving a decreased radius of curvature in a three dimensional figure.

In Figure 19, P_e indicates the position of the capillary for edge potential measurement. In each case, the attempt was made to place the outside radius of the capillary tip tangent to the edge being measured. This left the capillary opening normal to the electrode surface and directed toward that surface. P_c indicates the position of the capillary for potential measurements in the center of the electrode surface.

Data obtained using these elctrodes in found in Table III.

DISCUSSION

The higher ΔE value for configuration B compared to A under the same condition (runs 7 and 8 versus 12, 13, and 14) seems to be correlated with the geometry of the electrodes. In particular, there seems to be an inverse relationship between the radius of curvature and the potential gradient. The fact that the electrode reactions begin at points of small radius of curvature and move towards areas of infinite radius of curvature (see Fig. 14, 15) is visible evidence for this effect. Had we been able to make measurements over the conical surface of electrode C a more precise relationship might have been shown. A dual capillary measuring system which will be discussed in the proposed work section of this report should make such measurements possible.

The ΔE measured for plates undergoing reduction was somewhat less and opposite in sign to that measured for plates undergoing oxidation (see Table III Runs 7 and 13). Consideration of the overpotential as a potential tending to oppose the reaction which is occurring indicates that the signs of the ΔE's are the expected signs.

A decrease in current density is accompanied by a proportional decrease in the measured ΔE as shown in runs 15 and 16. The visible edge effect is also much less pronounced at low current densities. Compare Fig. 10 and 11, 12 and 13.

To demonstrate that the ΔE was not associated with the increasing thickness of the oxide layer built up during the course of electrode oxidation, measurements on run 14 were made over an 8 min. time period. These measurements included most of the Ag(I) stage of electrolytic oxidation. The ΔE values are plotted in Fig. 20. As this figure shows, there is no apparent trend in the ΔE values with time. The fact that similar ΔE values were observable on a platinum plate anodized to a potential sufficient to oxidize H_2O lends support to the contention that the ΔE is not caused by the formation of an oxide layer which is thicker at the edge than at the center.

Experiments in which overpotential was measured as a function of current density also indicate that the relation of E to i is not entirely ohmic. Sintered Ag plates made by Yardney and by us were oxidized at constant current using a Zn grid counter electrode in 0.1 N KOH saturated with ZnO. The Ag potential was measured vs. a saturated calomel electrode by means of a Varian recorder. The current supplied by a Hewlett-Packard Model 881 AX power supply was set at 2, 4, 6, 8...16 ma and the potential recorded after each change. The current was then decreased in 2 ma steps until 2 ma was reached again. The plates were oxidized 1-2 minutes to give a Ag_2O coating so that the resistance of the plates would not change significantly during the run. Potential variation with current was as shown in Fig. 21.

From the current applied and the potential measured (this potential was the difference between the Ag-calomel potential with no current flowing and that with current flowing), the resistance of the Ag_2O coating was estimated. Although it was expected that this resistance (calculated upon the assumption that only IR overpotential is involved) would remain quite constant or increase with increasing current (since more Ag_2O was being produced) we found in all cases that the calculated resistance decreased as the applied current increased. These results suggest that activation overpotential as well as ohmic overpotential is involved in the oxidation of Ag to Ag_2O.

PROPOSED WORK

To improve the accuracy and widen the scope of our ΔE measurements on electrode surfaces a new experimental apparatus must be built. The design will include the following:

1. A larger test cell using two capillary sensing electrodes which would take simultaneous potential measurements. Much better control of electrode position would then be possible because no electrode or capillary movement would be involved in making ΔE measurements. Measurements of ΔE over a complex geometry such as the cone electrode which has been previously mentioned could also be made.

2. A more sensitive null device would make the use of smaller capillary electrodes feasible. Greater sensitivity of ΔE measurements would also be available.
3. An improved constant current device to replace the battery-high resistance system.

With the improved instrumentation, a more quantitative consideration could be given to all previously mentioned variables in addition to the following:

1. Electrolyte composition and concentration
2. The effect of electrode composition and structure (Platinum electrodes have already been tested (Table II, run 10)
3. Position of test electrodes relative to counter electrode position
4. Capillary size
5. Movement of electrolyte such as convection and stirring

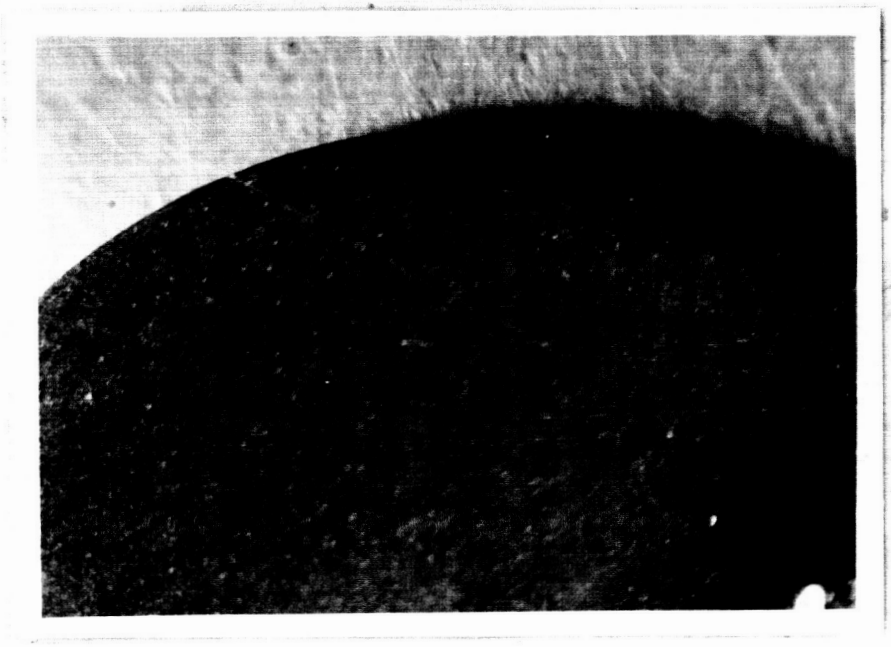

Fig. 1-A Cleaned silver foil electrode (unpolished)

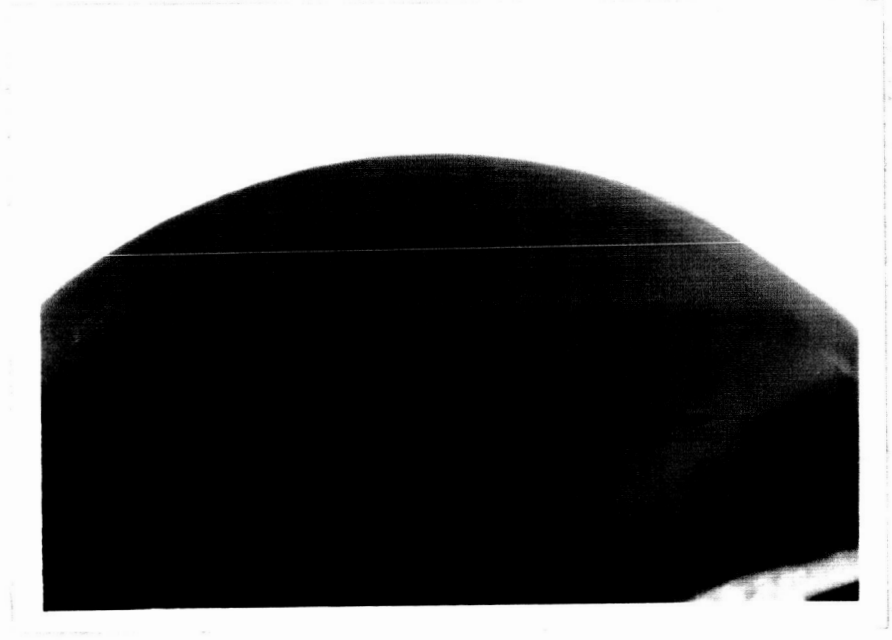

Fig. 1-B Polished silver foil electrode

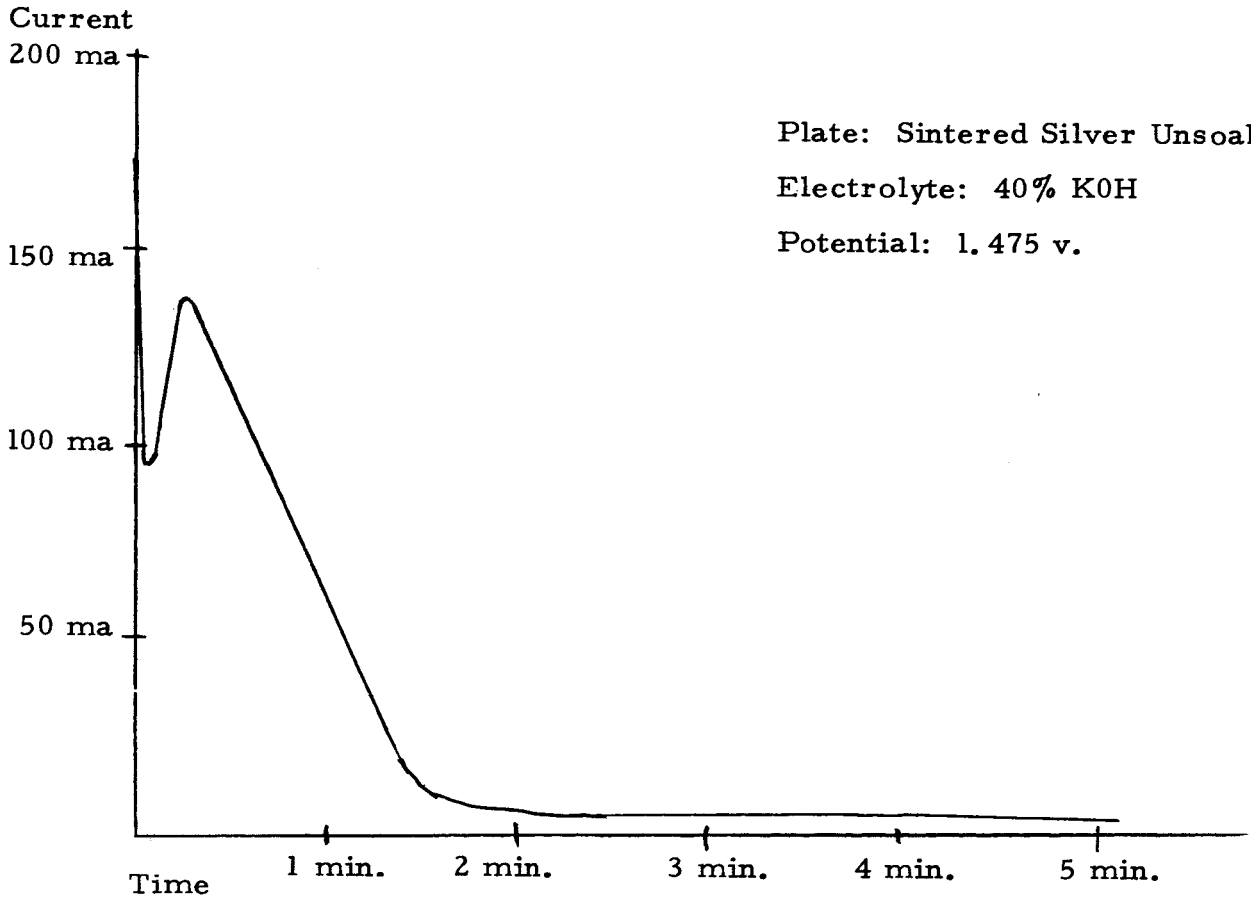

Figure 2

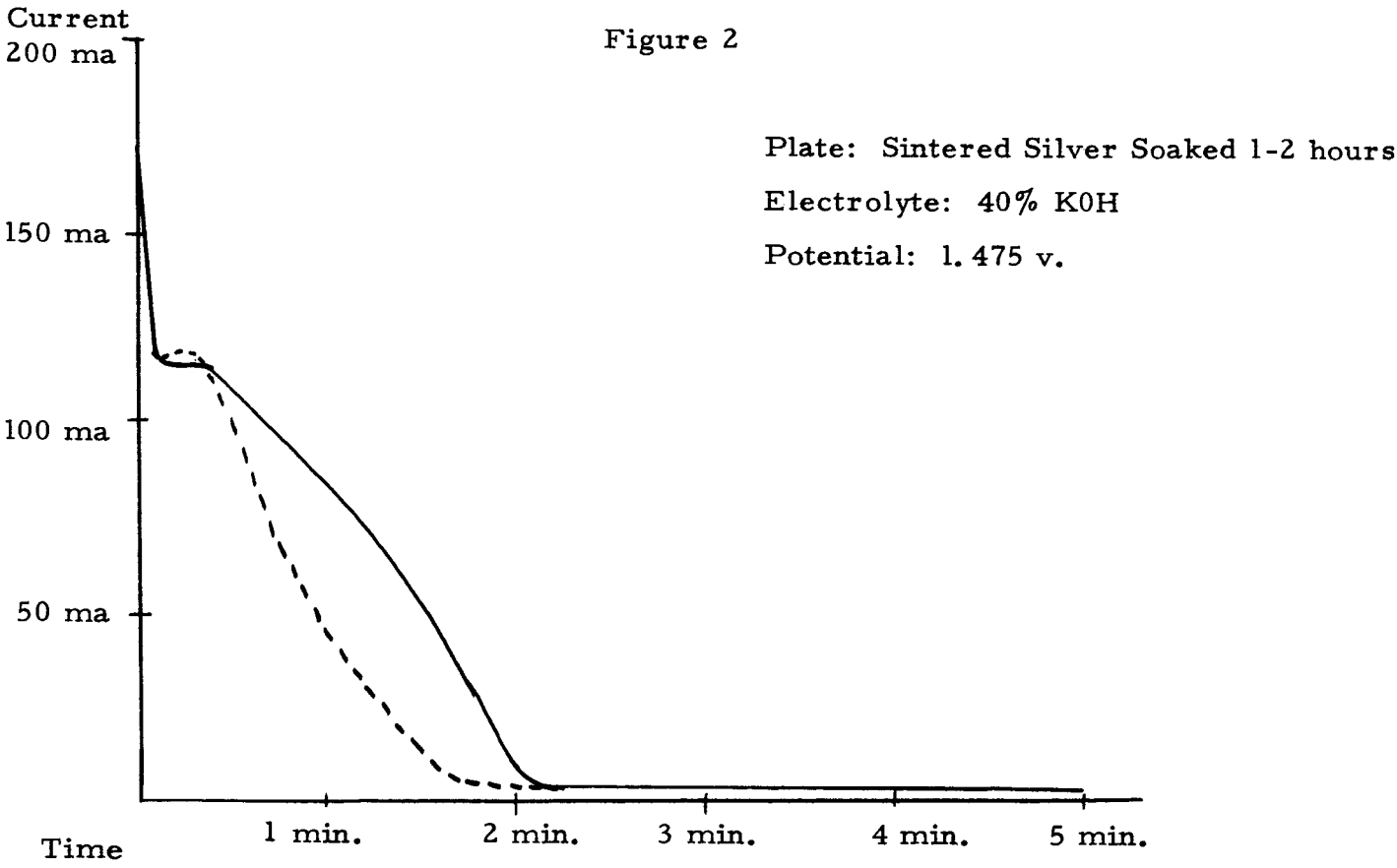

Figure 3

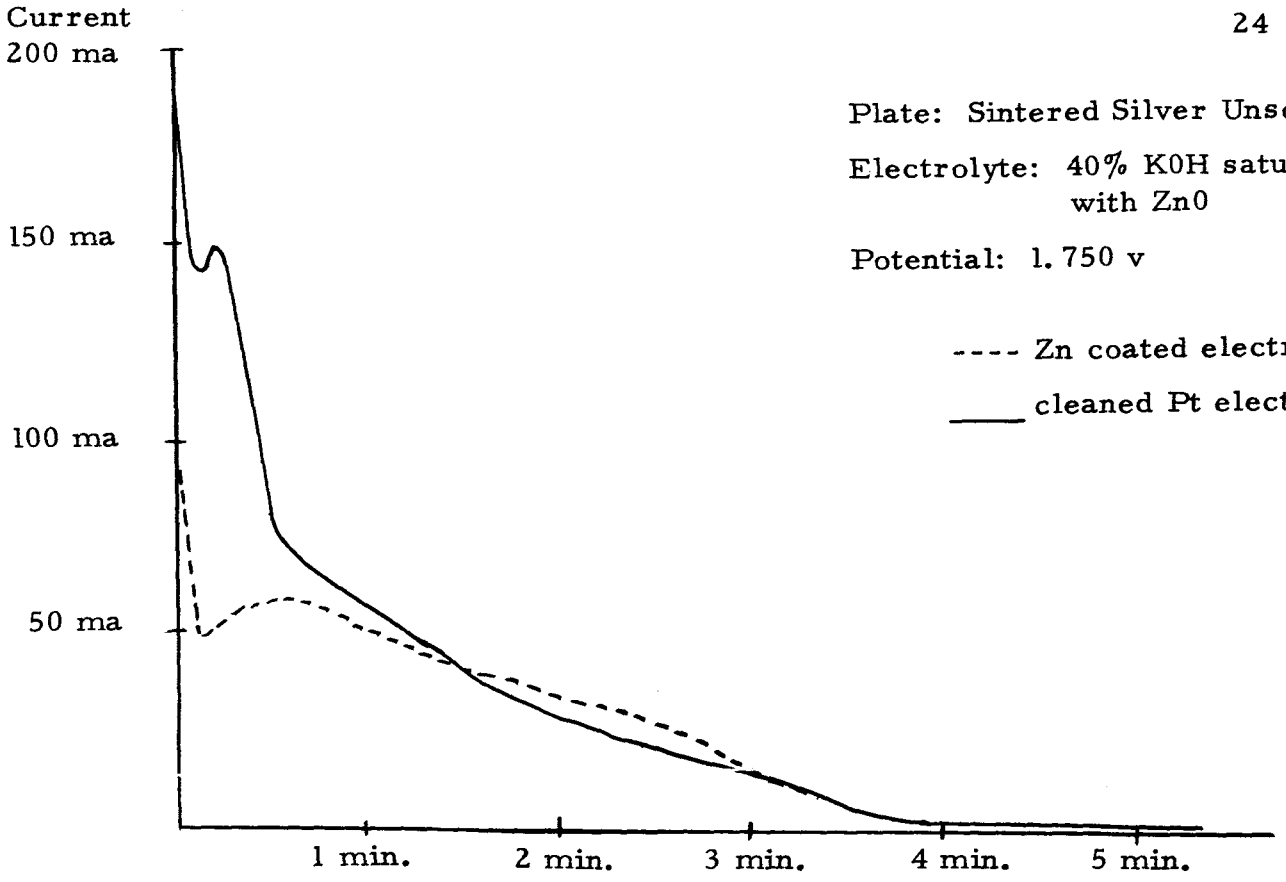

Figure 4

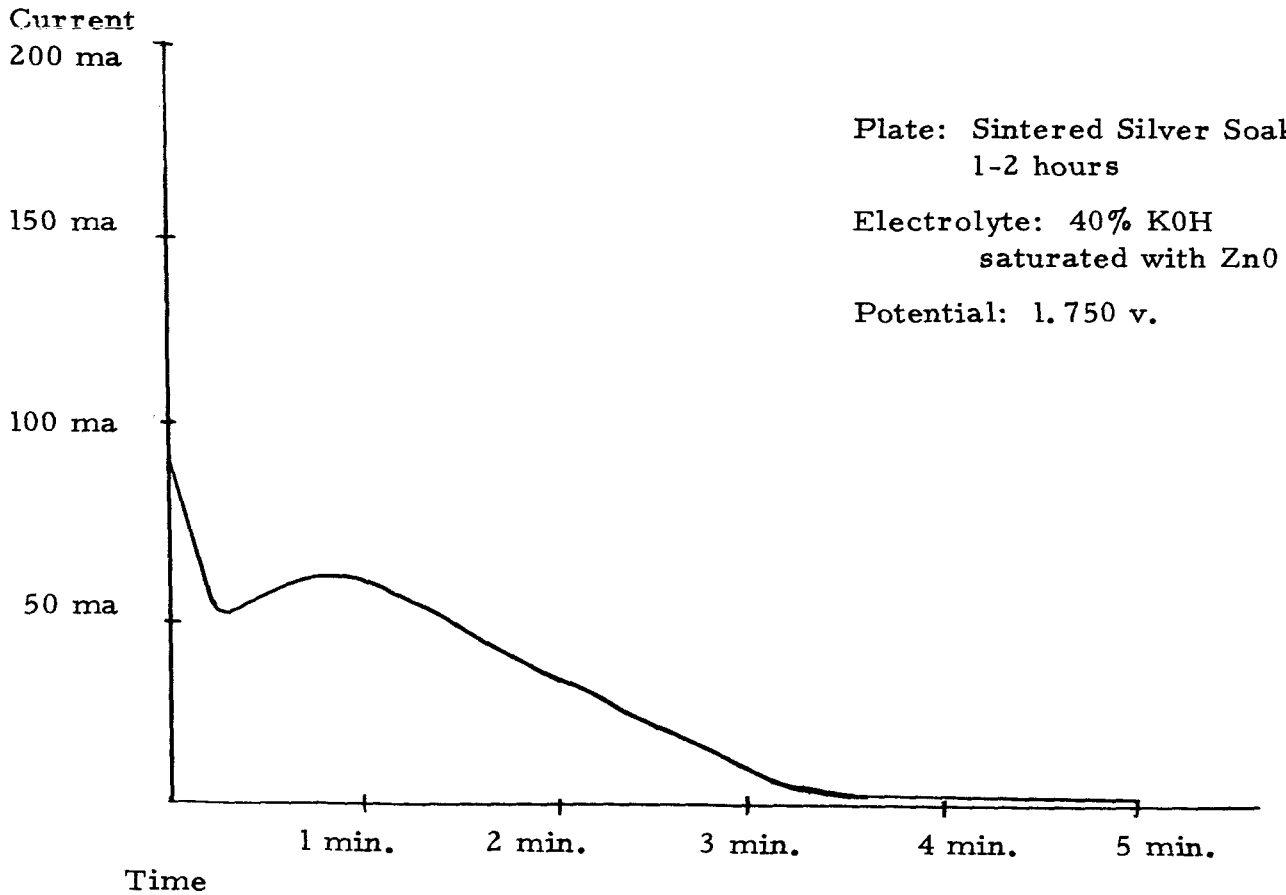

Figure 5

Potential versus time curve obtained in the oxidation of silver electrodes at constant current

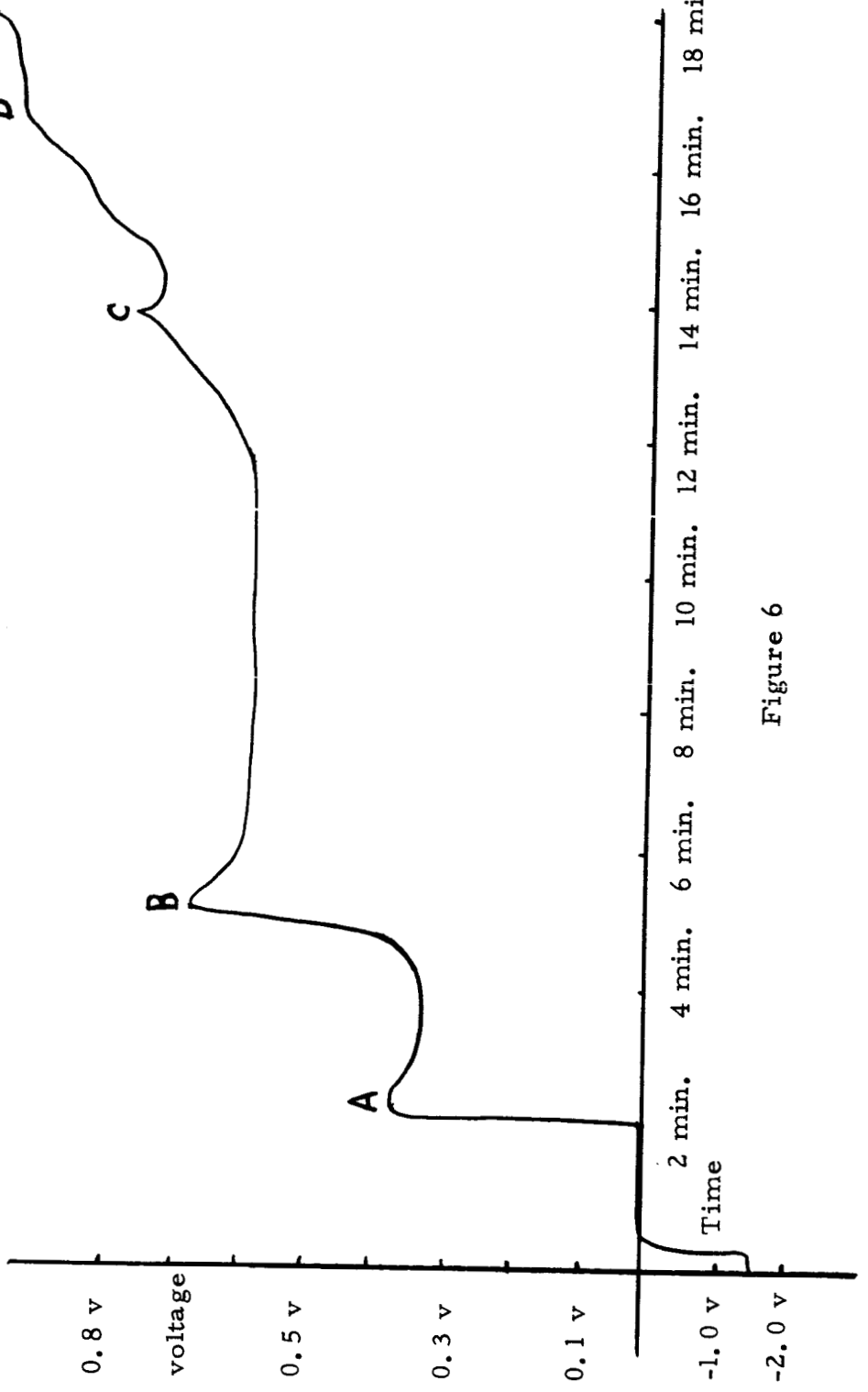

Figure 6

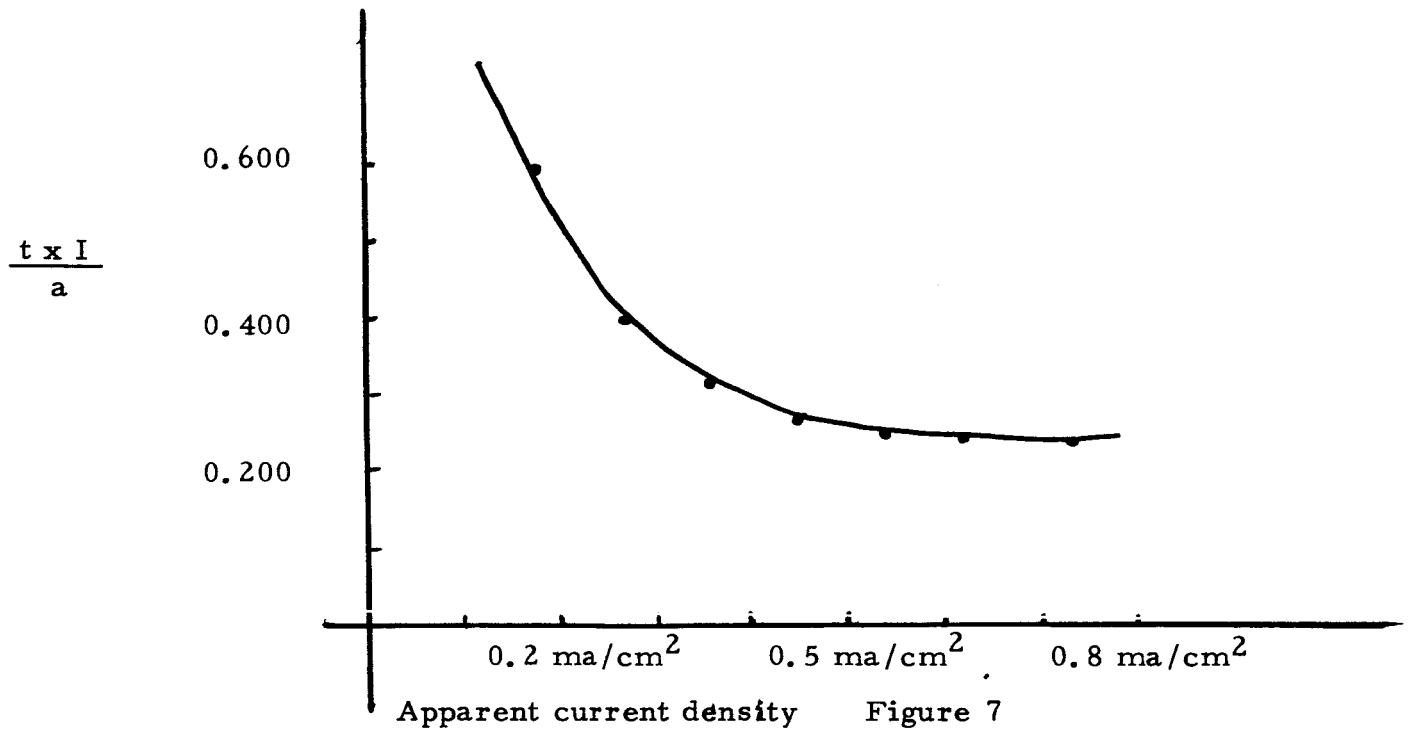

Figure 7

Linear and logarithmic plots of the charge per unit area vs apparent current density

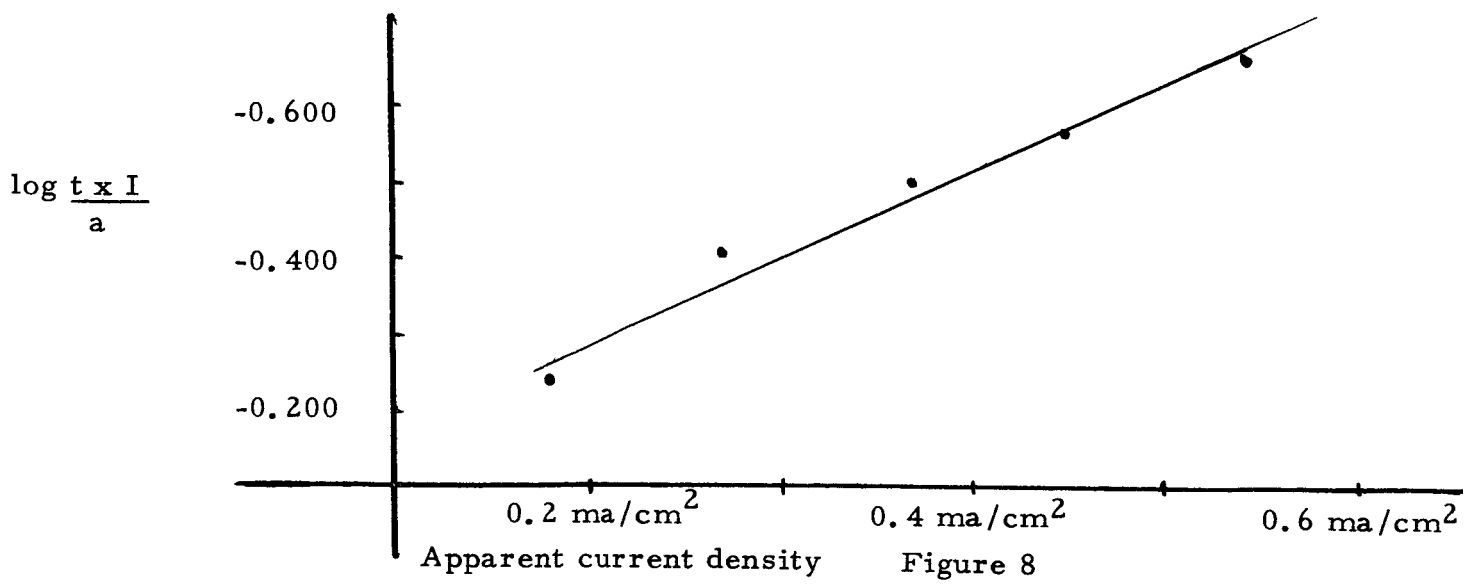

Figure 8

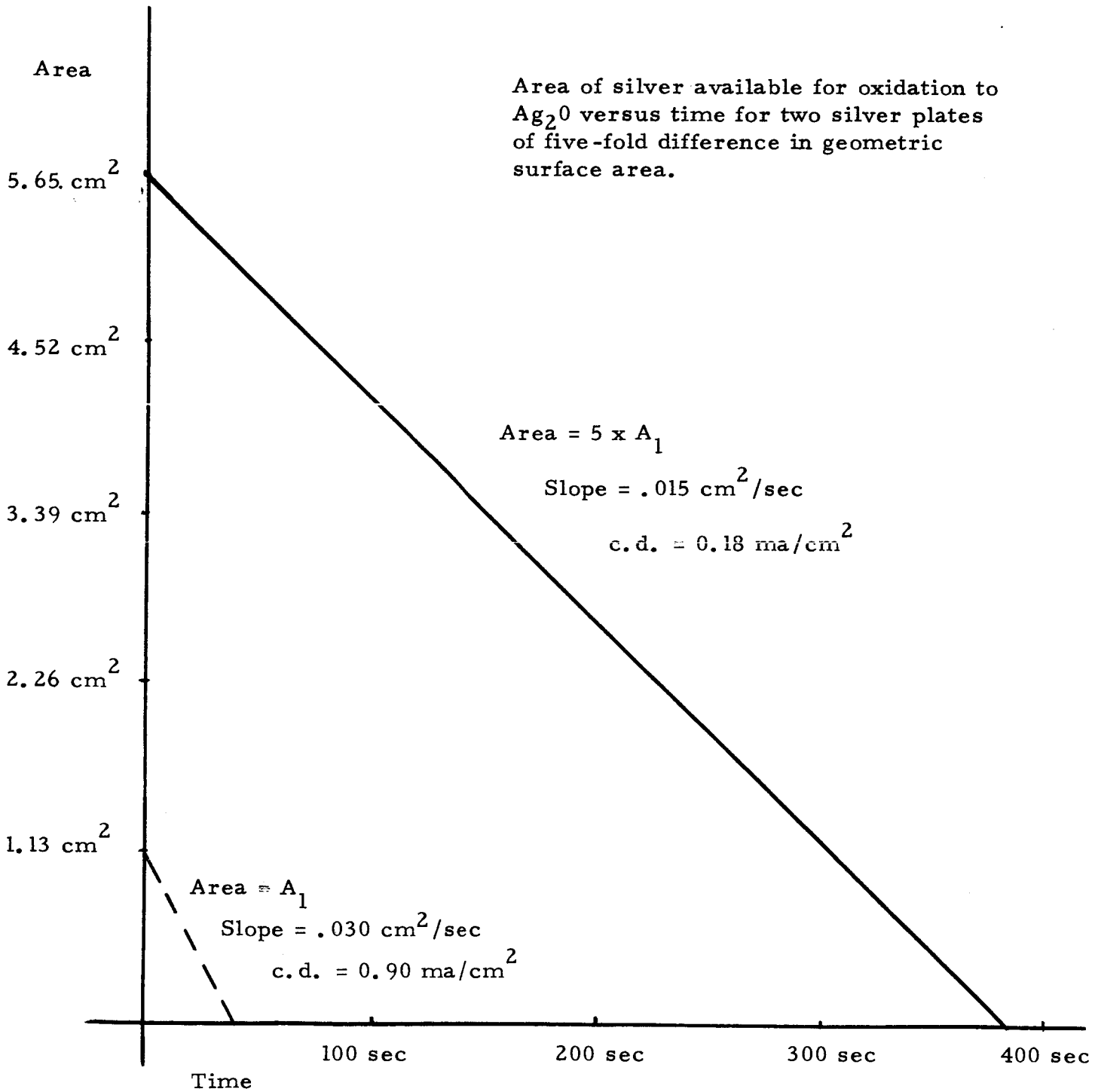
Area
5.65 cm2
4.52 cm2
3.39 cm2
2.26 cm2
1.13 cm2
Area of silver available for oxidation to Ag2O versus time for two silver plates of five-fold difference in geometric surface area.
Area = 5 x A1
Slope = .015 cm2/sec
c.d. = 0.18 ma/cm2
Area = A1
Slope = .030 cm2/sec
c.d. = 0.90 ma/cm2
100 sec
200 sec
300 sec
400 sec
Time

Figure 9

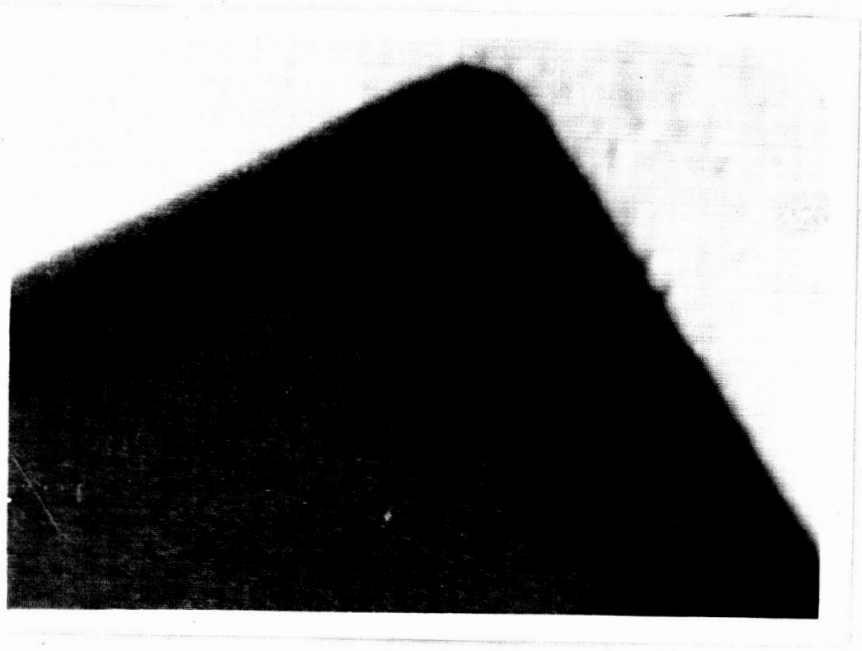

Fig. 10 Ag electrode (configuration A) oxidized at .2 ma/cm^2

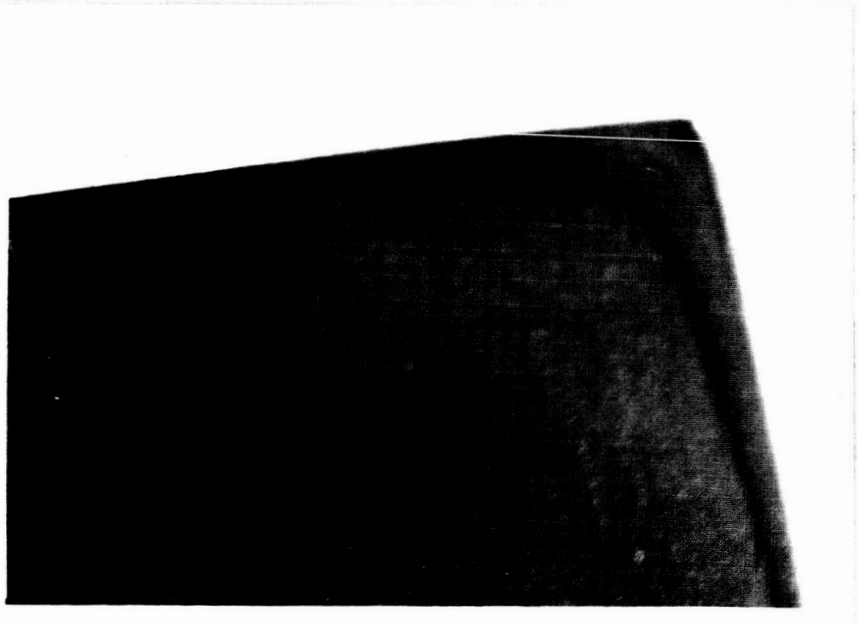

Fig. 11 Ag electrode (configuration A) oxidized at 60 ma/cm^2

Fig. 12 Ag electrode (configuration A) reduced at .2 ma/cm^2

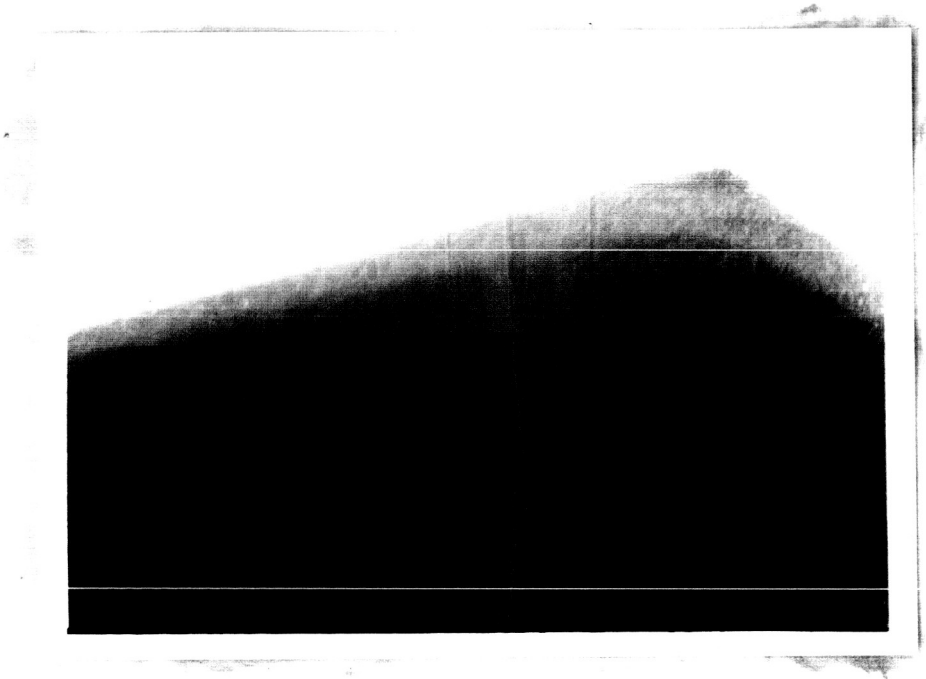

Fig. 13 Ag electrode (configuration A) reduced at 60 ma/cm^2

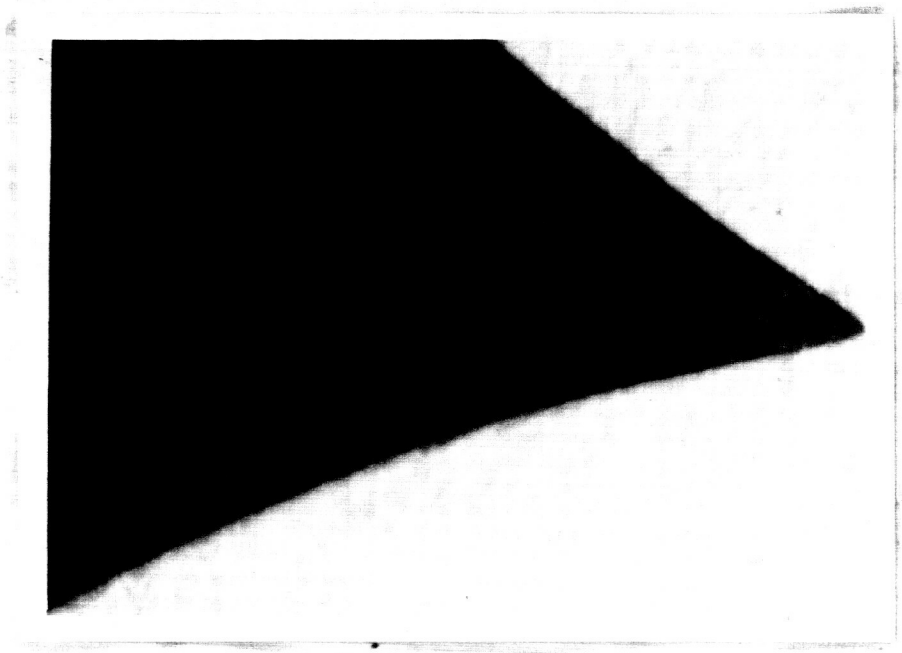

Fig. 14 Ag electrode (configuration B) oxidized at 60 ma/cm^2

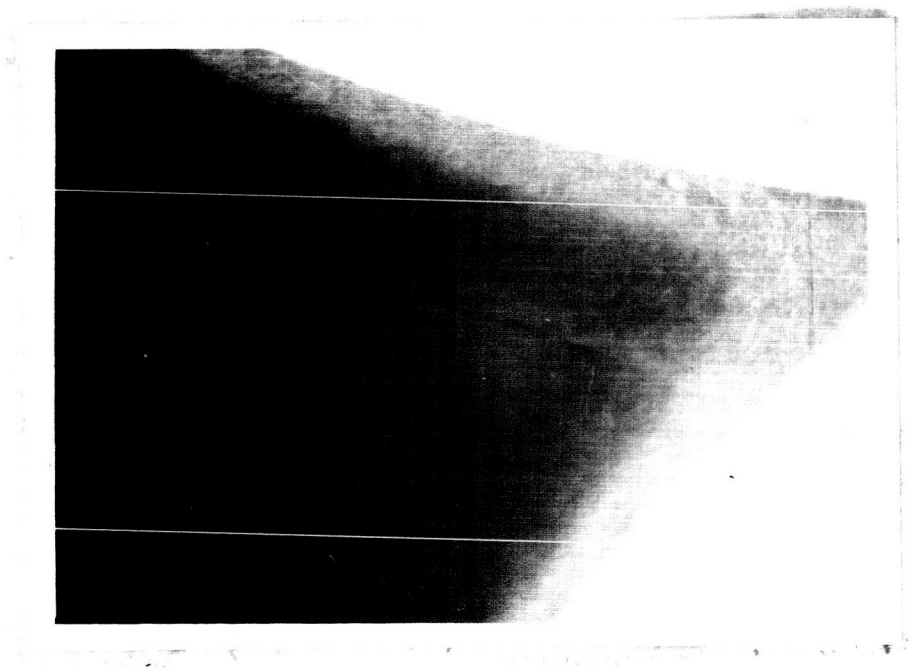

Fig. 15 Ag electrode (configuration B) reduced at 60 ma/cm^2

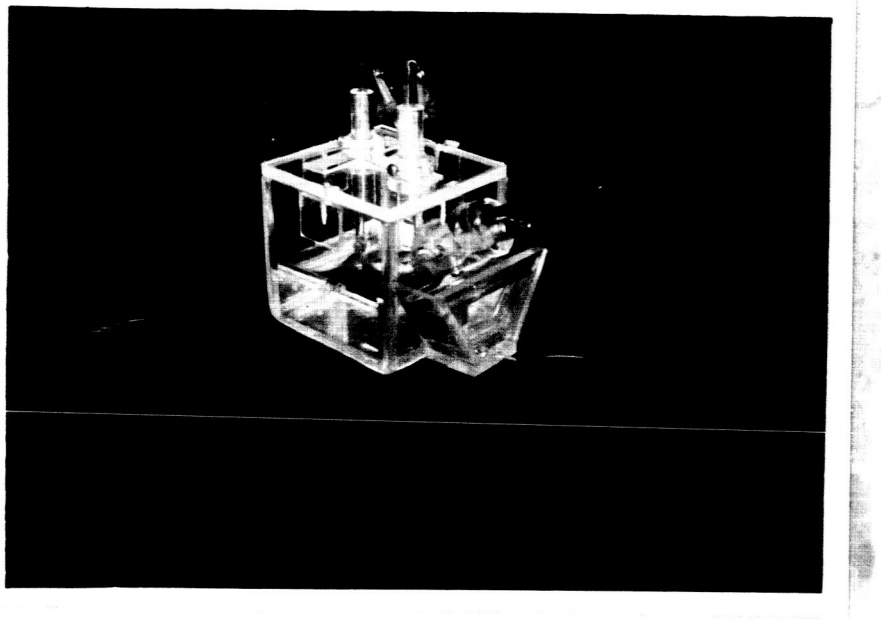

Fig. 16 The Test Cell

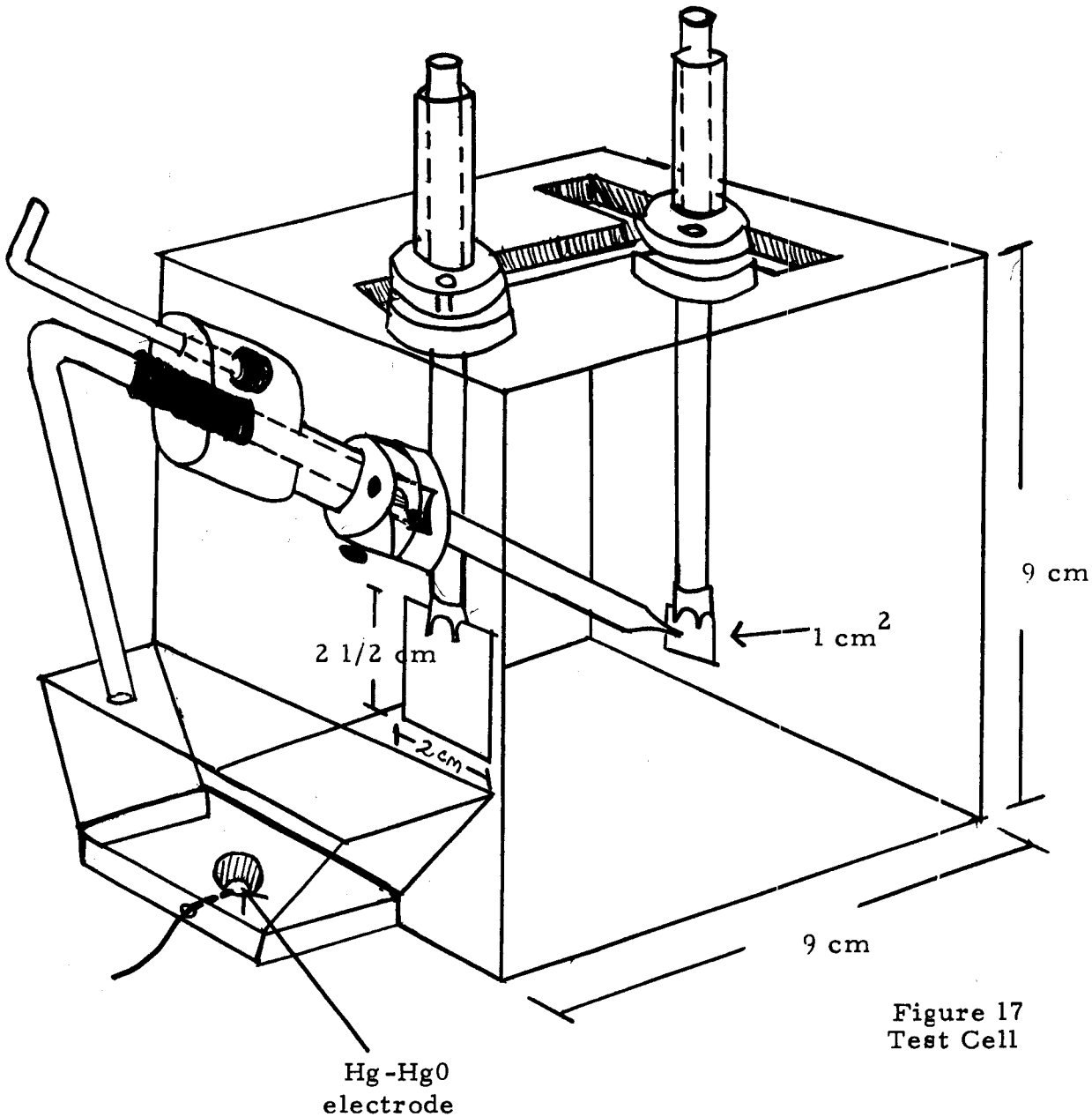

Figure 17
Test Cell

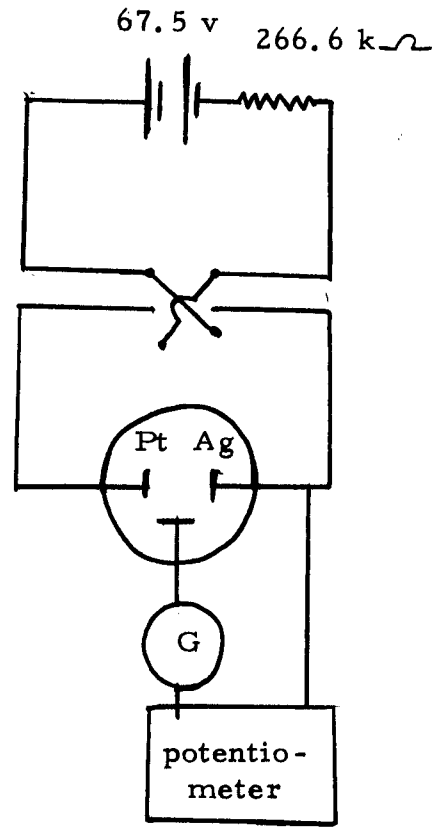

Figure 18
Circuit Diagram

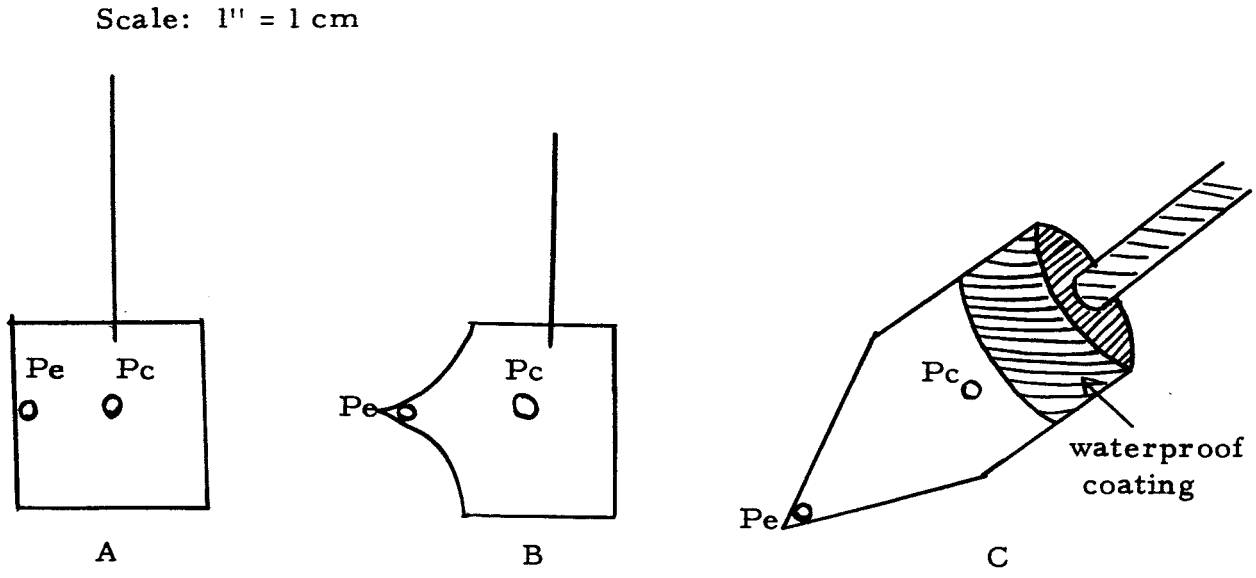

Fig. 19 Test Electrode Configurations

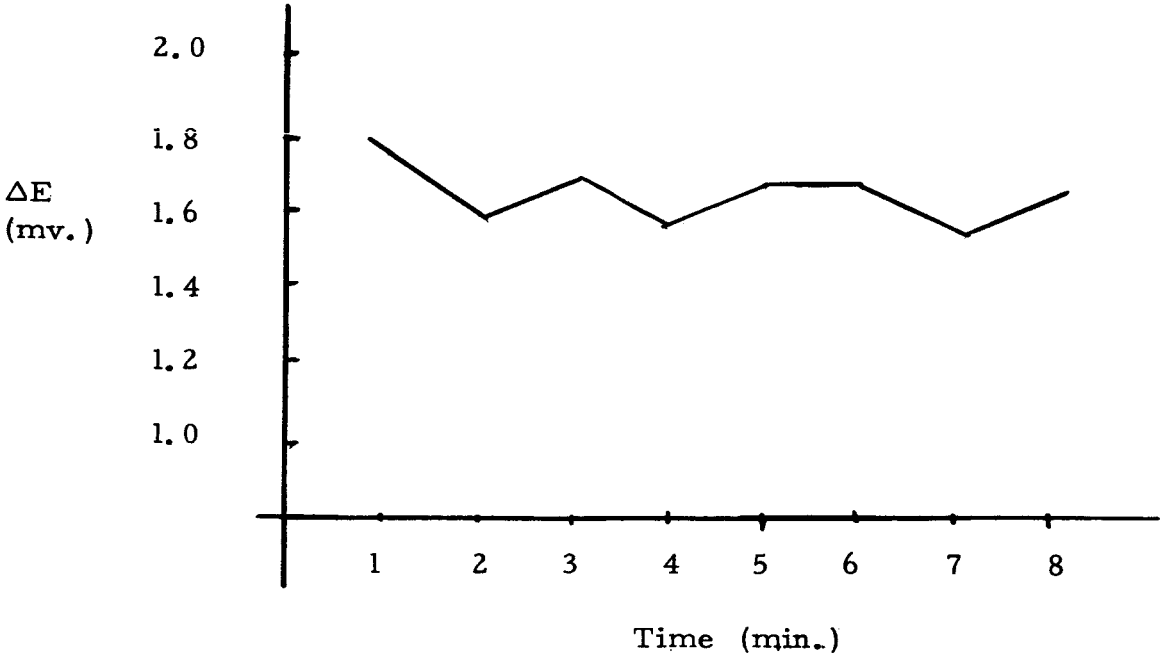

Fig. 20 ΔE as a function of time (oxide film) (Run 14 Table III)

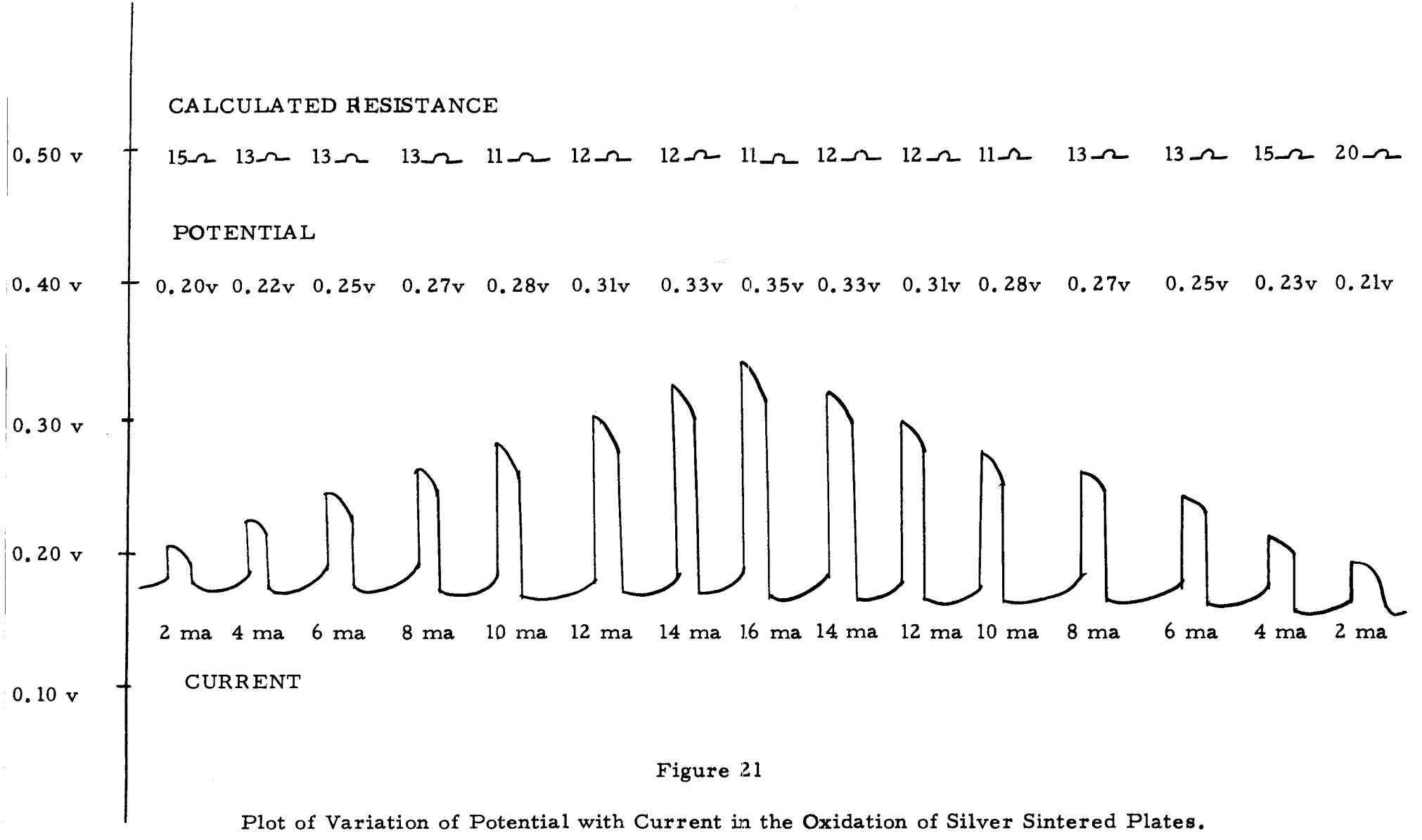

Figure 21

Plot of Variation of Potential with Current in the Oxidation of Silver Sintered Plates.

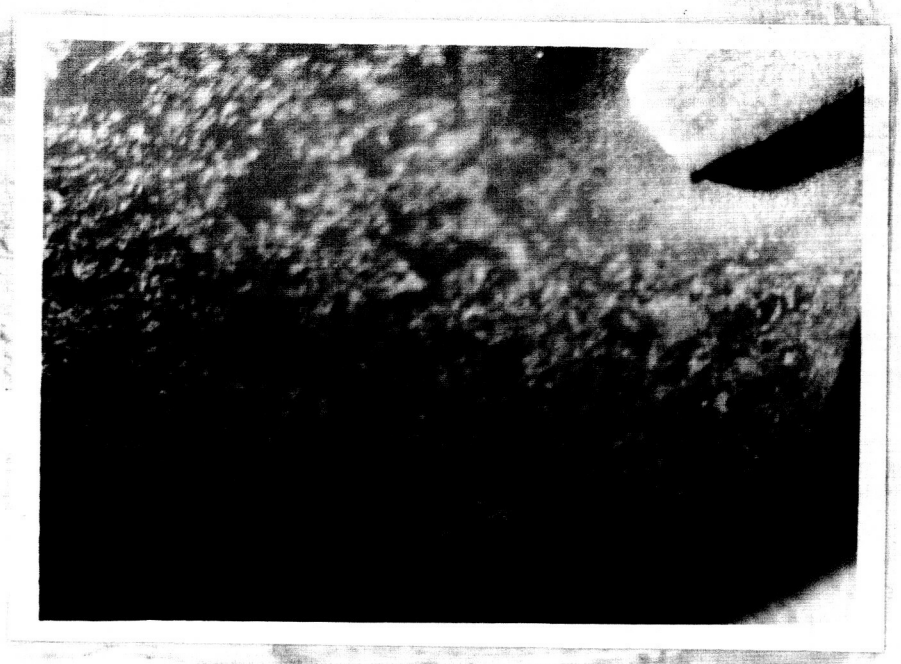

Fig. 22-A
Oxidation pattern observed on most unpolished and some polished plates.

Fig. 22-B
Spotty oxidation observed on plates which had been polished (indicating some protected areas)

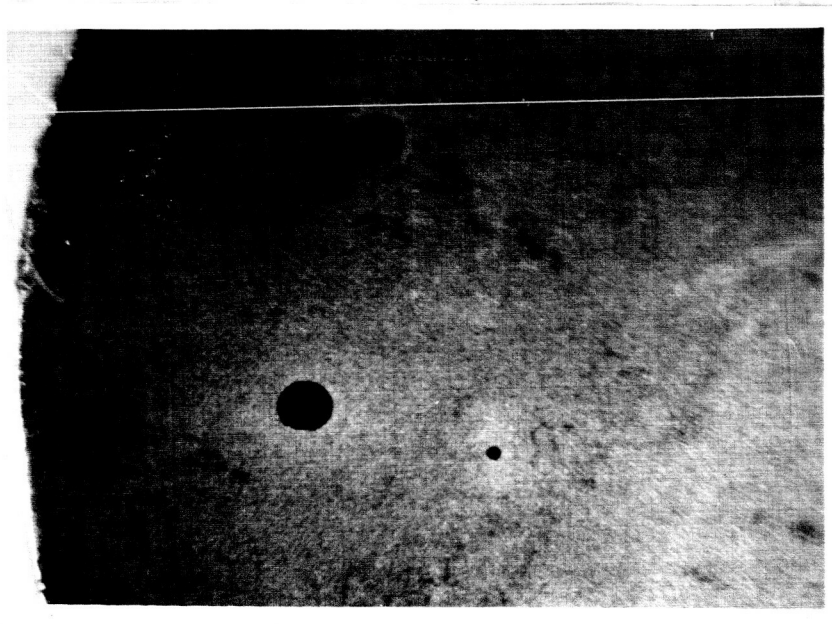

Fig. 22-C
Same as 22-B

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